学校编码:10384
学号:20520071150970

密级_____
UDC_____

厦门大学

硕 士 学 位 论 文

土壤中 POPs 的污染评价及行为研究

Contamination Status and Behavior of POPs in Soil

刘 征 侃

指导教师姓名:王秋泉 教授

专 业 名 称:分析化学

论文提交日期:2010 年 12 月

论文答辩时间:2010 年 12 月

学位授予日期:2010 年 12 月

答辩委员会主席:_____

评 阅 人:_____

2010 年 12 月

Contamination Status and Behavior of POPs in Soil

A Thesis Presented

by

Zhengkan Liu

Supervisor: Professor Qiuquan Wang

Submitted to the Graduated School of Xiamen University

for the Degree of Master of Science

Dec 9, 2010

Department of Chemistry, Xiamen University

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摘 要

结合本研究小组以前的工作，建立了土壤中 POPs 的 pLVI-GC/ECNI-qMS 和 GC/EI-qMS 分析方法，用于测定土壤样品中的痕量 POPs（包括 OCPs、PCBs、PBDEs 和 PAHs），该方法检出限低、准确度高，符合本研究工作要求。

利用所建立土壤样品中 POPs 的分析方法，对我国九个城市表层土壤中 POPs 进行了检测，评价了这些地区土壤 POPs 的污染状况，分析判定了这些地区 POPs 的污染来源。依据统计学原理，提出了相似系数（$\cos\theta$）这一概念，通过计算样品与污染源之间相似系数并进行比较来判断 H-POPs 可能的污染来源。这种污染源判断方法简便易行，首次定量描述了样品中的 H-POPs 与其污染源之间的相似程度，避免了由主观判断引入的偏差，可以作为很好的 POPs 污染来源判断方法。

中国大陆九个城市表层土壤中Σ_9OCPs、Σ_{10}PCBs、Σ_{15}PBDEs 和Σ_{18}PAHs 的总干重浓度分别为 1.64-3.21、0.16-0.97、0.26-3.16 和 608-1685 ng/g。北方城市（鞍山、北京、乌鲁木齐）土壤中 POPs 含量相对于其他南方城市都较高，原因除了工业生产、燃煤取暖等本地污染来源外，POPs 经过大气长距离传输后在温度较低的北方发生沉积和富集也是这些地区 POPs 污染较严重的一个重要原因。通过典型 POPs 比值和相似系数计算比较，这些城市 POPs 的污染来源较为一致，林丹、DDTs 的历史使用、tri-PCB 产品、deca-BDE 产品和石油产品使用分别为土壤中 HCHs、DDTs、PCBs、PBDEs 和 PAHs 的主要污染来源。九个城市土壤样品中Σ_9OCPs、Σ_{10}PCBs、Σ_{15}PBDEs、Σ_{18}PAHs 总浓度分别与各城市 GDP（2008 年）存在一定程度线性正相关（r = 0.342、0.619、0.641 和 0.279），表明我国社会经济发展的同时不可避免地带来了 POPs 的污染问题。α/γ-HCH 与纬度正相关（r＝0.821），表明目前我国 HCHs 的空间分部状况主要取决于环境残留 HCHs 的重新蒸馏再分配行为。

测定了福建省天宝岩自然保护区土芯样品中的 POPs 浓度，天宝岩土壤 POPs 污染水平低于世界大多数地区，可认为是环境背景地区进行研究。通过典型 POPs 比值和相似系数计算，林丹、DDTs 的历史使用、tri-PCB 产品、deca-BDE

产品和石油产品使用被分别认为是土壤中 HCHs、DDTs、PCBs、PBDEs 和 PAHs 的主要污染来源。通过逸度分数计算评价了 POPs 在天宝岩表层土壤中的土壤-大气分配，该分配过程与它们辛醇-空气分布系数（K_{OA}）之间有着密切的关系：对于 $\log K_{OA} < 9$ 的 POPs，它们的逸度分数几乎都 > 0.5，指示为从土壤至大气的净挥发，它们在该地区土壤-大气分布过程中扮演了“二次来源（secondary source）”的角色；对于 $\log K_{OA} > 9$ 的 POPs，它们的逸度分数都 < 0.5，指示为从大气至土壤的净沉积，也即天宝岩土壤依然作为它们在这两种环境介质之间分布的“汇（sink）”。

POPs在土芯中浓度的基本趋势都是随着深度减小而增大，Σ_9OCPs、Σ_{10}PCBs、Σ_{15}PBDEs、Σ_{18}PAHs的浓度分别从78-89 cm 中的0.036、0.015、0.011、65.56 ng/g增加到表面0-3 cm中的0.70、0.085、0.12、141.3 ng/g。从它们的纵向分布我们可以得知：天宝岩环境中OCPs正在逐渐减少，PCBs/PBDEs的污染输入依然存在，并且PCBs的污染输入近年来已经逐渐减少，而PBDEs的污染输入在不断增多；天宝岩环境中PAHs污染水平则保持着不断提高的趋势。对POPs在天宝岩土芯中的纵向分布进行了研究，POPs的历史排放和它们的辛醇-水分布系数（K_{OW}）都会影响POPs在土芯中纵向分布和组成。POPs在天宝岩土芯中纵向迁移的方式主要为随着水流运动，由于不同K_{OW}的POPs迁移能力不一致，这种纵向迁移会改变不同深度中POPs的组成，并且影响它们与各自污染来源之间的相似系数。

关键词：POPs；土壤；大气；污染评价；GC/MS

Abstract

Based on our previous studies, an analytical method using pLVI-GC/ECNI-qMS for H-POPs (including OCPs, PCBs and PBDEs) and GC/EI-qMS for PAHs accumulated in soil was firstly established.The method established has the charateristics of low detection limits and high accuracy.

The surface soil samples were collected from 9 cities of China and the POPs in them were determined. The POPs contamination status and possible sources of the soil from those cities was evaluated. Based on the principle of statistics, the concept of similarity coefficient (cosθ) was firstly recommended evaluatingthe possible sources of the H-POPs in the soil. This method was simple, and could quantitatively describe the relationship between the H-POPs in the soil and those in their technical products. It was thus expected to be valuable for tracing the H-POPs sources in the soil.

Total concentrations of Σ_9OCPs, Σ_{10}PCBs, Σ_{15}PBDEs and Σ_{18}PAHs were determined to be 1.64-3.21, 0.16-0.97, 0.26-3.16 and 608-1685 ng/g dry weight in the soil samples collected from the 9 cities, respectively. It was noticed that levels POPs in the soil from the cities in north part of China (Anshan, Beijing, Wulumuqi) were higher than those in soil from the cities in south part of China. The reasons for this situation might be, on one hand, the local industry and burning for heating during winter time in these places; on the other hand, POPs transferred from remote places via long range atmospheric transport (LRAT) accumulated in the cold north. The possible sources of POPs in the soil from these cities were determined, historical usage of HCHs, DDTs and tri-PCB technical product, recent usage of lindane and deca-BDE technical product and usage of petroleum product were considered the major sources of those HCHs, DDTs, PCBs, PBDEs and PAHs, respectively. The soil POPs concentrations have linear relationship positively with gross domestic production (GDP in 2008) of the cities, with the correlation coefficients of 0.342, 0.619, 0.642 and 0.279 for the Σ_9OCPs, Σ_{10}PCBs, Σ_{15}PBDEs and Σ_{18}PAHs,

respectively. Moreover, the hexachlorocyclohexane (HCH) isomer ratio of α/γ-HCH were fractionated with latitude indicating the spatial distribution of HCHs in China is now governed by the nationwide redistillation of the HCHs residues used in the past but not by their recent use patterns.

Contentrations of POPs in the soil-core sampled at Tianbao Rock National Natural Reservation located in southeastern China were determined and the concentrations were much lower than those from most of other places in China and in the world. Thus we could consider POPs level there as the background level to most of the places on the earth. Recent usage of lindane, historical usage of DDTs, penta-PCB product, deca-BDE product and usage of petroleum product were considered the major sources of HCHs, DDTs, PCBs, PBDEs and PAHs there, respectively. For POPs in the surface soil, there was a decreasing trend for fugacity fraction (*ff*) along with increase of their corresponding K_{OA}, which implied that K_{OA} was an important parameter controlling POPs partition between soil and air in Tianbao Rock. For POPs with $\log K_{OA} < 9$, their *ff* was almost larger than 0.5 indicating net volatilization to air. This observation suggested the POPs in the soil from Tianbao Rock act as a secondary source for the pullotion of other places; for the POPs with $\log K_{OA} > 9$, their *ff* was smaller than 0.5 which indicated net deposition to soil, suggesting that soil still act as a sink for the POPs in the area.

There were general increasing trends for POPs levels along with decrease in the depth of the soil-core sampled in Tianbao Rock. Concentrations of Σ_9OCPs, Σ_{10}PCBs, Σ_{15}PBDEs and Σ_{18}PAHs increased from 0.036 in the depth of 78-89 cm to 0.70 ng/g in the top 3 cm, 0.015 to 0.085 ng/g, 0.011 to 0.12 ng/g and 65.56 to 141.3 ng/g, respectively. It was inferred that OCPs in the soil of Tianbao Rock began to reduce in recent years due to forbidden for a long time and degradation of those already existed in the environment; however, the input of PCBs has decreased in recent years than before meanwhile the input of PBDE were being enhanced; PAH contamination level in the Tianbao Rock was continuously increasing. Historical emission and the K_{OW} of POPs could together influence the vertical distribution of them in the soil-core. The major vertical migration style of POPs in the soil-core was transportation with water

movement. Since the soil-core could act as a chromatographic column separating compounds according to their K_{OW}, composition of POPs in the soil-core would vary along with different depth, and thus the cosθ between them and their corresponding technical sources were also influenced.

Key words: POPs; Soil; Air; Contamination Evaluation; GC/MS

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第一章 前言

1.1 大气持久性有机污染物

持久性有机污染物（persistent organic pollutants，POPs）是指具有环境持久性、生物蓄积性、半挥发性、高毒性的有机污染物。POPs可以通过大气、洋流等方式在全球范围内循环，它所造成的污染问题已成为全球性的环境问题，因此在最近数十年成为环境科学研究的热点。2001年5月，国际社会共同签署了《斯德哥尔摩公约》，将三大类共十二种化合物列入公约受控范围，其中包括：艾氏剂（aldrin）、狄氏剂（dieldrin）、异狄氏剂（endrin）、滴滴涕（dichlorodiphenyl trichloroethane，DDT）、灭蚁灵（mirex）、毒杀芬（toxaphene）、氯丹（chlordane）、七氯（heptachlor）、六氯苯（hexachlorobenzene，HCB）这九种有机氯杀虫剂（organochlorinated pesticide，OCPs），PCDDs和PCDFs两种工业污染物，以及两种化工产品多氯联苯（polychlorinated biphenyls，PCBs）类和HCB（既是农药又是化工产品）[1]，旨在全球范围内对它们进行控制和削减。《斯德哥尔摩公约》是开放性的，2009年5月举行的斯德哥尔摩公约缔约方大会第四届会议决定将全氟辛基磺酸及其盐类、全氟辛基磺酰氟、商用五溴联苯醚、商用八溴联苯醚、开蓬、林丹、五氯苯、α-HCH、β-HCH、六溴联苯等九种化学物质新增列入公约，标志着这些化合物也将被缔约方禁止生产和使用，这对减少环境压力，降低污染水平具有十分重要的意义[2]。

POPs可以广泛分布于各种环境介质中，在全球范围内大气、土壤、沉积物、水体、植物等环境介质中都已检测到POPs的存在[3]。由于POPs的半挥发性，大气循环成为POPs在全球范围内空间分布的最主要途径，并且大气POPs由于人的呼吸作用而与人体健康之间关系最为密切，因此受到最为广泛的关注。在本章中，针对近年来关于大气POPs的研究中人们所关注的新污染物、采样方法、检测技术、评价方法进行了综述。